IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of: Ken-ichi Machida et al

Serial Number: 10/560,831 Group Art Unit: 1793

Filed: 11/01/2006 Examiner: SHEEHAN, JOHN P

For RARE EARTH-IRON-BORON BASED MAGNET AND METHOD FOR PRODUCTION THEREOF

DECLARATION UNDER 37 CFR 1.132

Commissioner for Patents
Washington, D.C. 20231

Sir:

Ken-ichi Machida, a citizen of Japan, hereby declare and state:

1. I have got a degree (Doctor of Engineering) in the field of applied chemistry which was conferred upon me by Osaka University, in Osaka, Japan, in March of 1982.

2. I have been employed by Osaka University as since 1990 and now I am a professor of The Center for Advanced Science and Innovation, Osaka University. In April of 1982, I started my research works as an assistant professor in the fields of Electrochemistry and Catalysis at Hokkaido University. In May of 1990, I returned to Osaka University and worked as the associate professor in Materials Science and Applied Chemistry. Finally, I promoted to the professor of The Center for Advanced Science and Innovation in April of 2000. Up to date, I have been mainly studying on magnetic materials such as Nd-Fe-B permanent magnets as well as optical materials such as phosphors, catalysts, microwave absorbing materials, and so on.

3. I am a member of the following societies:
   1) The Electrochemical Society (USA)
   2) The Japan Institute of Metals
   3) The Magnetics Society of Japan
   4) The Institute of Electrical Engineers of Japan
   5) The Rare Earth Society of Japan
   6) The Chemical Society of Japan
   7) The Japan Society of Applied Physics
   8) The Ceramic Society of Japan
   9) Catalysis Society of Japan
   10) The Japan Society of Powder and Powder Metallurgy

4. My papers relating to the magnetic materials as published since 2005 are as follows:

1) J.-R. Liu, M. Itoh, and **K. Machida**, “Electromagnetic Wave Absorption Properties of $Fe_{1-x}Co_x/Y_2O_3$ (x=0.33, 0.5 0.67) Nanocomposite in Gigahertz Range,” *J. Alloys Comp.*, **389**, 265-269 (2005).
2) T. Horikawa, K. Miura, M. Itoh, and **K. Machida**, “Characterization and Microwave Absorbing Properties of Nd-Fe-Ti Intermetallic Compounds Derived from Nd-Fe-B Sintered Magnet Scraps,” *IEEE trans. Mag.*, **41(6)**, 2064-2070 (2005).
3) J.-R. Liu, M. Itoh, T. Horikawa, **K. Machida**, S. Sugimoto, T. Maeda, “Gigahertz range Electromagnetic Wave Absorbers Made of Amorphous-Carbon-based Magnetic Nanocomposites,” *J. Appl. Phys.* **98(9)**, 054305/1-054305/7 (2005).
4) **K. Machida**, J. R. Liu, and M. Itoh, “GHz Range Absorption Properties of -Fe/Y_2O_3, FeCo/Y_2O_3 and α-Fe/Fe_3B/Y_2O_3 Nanocomposites,” *IEEE Trans. Magn.*, **41(10)**, 3577-3579 (2006).
5) T. Horikawa, K. Miura, M. Itoh, and **K. Machida**, “Effective Recycling for Nd-Fe-B Sintered Magnet Scraps,” *J. Alloys Comp.*, **408-412**, 1386-1390 (2006).
6) D.-S. Li, T. Horikawa, J.-L. Liu, M. Itoh, and **K. Machida**, “Electromagnetic wave Absorption Properties of Iron/Rare Earth Oxide Composites Dispersed by the Amorphous Carbon Powders,” *J. Alloys Comp.*, **408-412**, 1429-1433 (2006).
7) M. Itoh, J.-L. Liu, T. Horikawa, and **K. Machida**, “Electromagnetic Wave Absorption Properties of the Nanocomposite Powders derived from Intermetallic Compounds and Amorphous Carbon,” *J. Alloys Comp.*, **408-412**, 1400-1403 (2006).
8) J. R. Liu, M. Itoh, and **K. Machida**, “Frequency Dispersion of Complex Permeability and Permittivity on Iron-based Nanocomposites Derived from Rare Earth-Iron Intermetallic Compounds,” *J. Alloys Comp.*, **408-412**, 1396-1399 (2006).
9) K. Miura, M. Masuda, T. Horikawa, M. Itoh, **K. Machida**, “Microwave Absorption Properties of the Nano composite Powders Recovered from Nd-Fe-B bonded Magnet Scrap,” *J. Alloys Comp.*, **408-412**, 1391-1395 (2006).
10) J. R. Liu, M. Itoh, T. Horikawa, E. Taguchi, H. Mori, and **K. Machida**, “Iron based carbon nanocomposites for electromagnetic wave absorber with wide bandwidth in GHz range” *Appl. Phys. A,* **82(3)**, 509-513 (2006).
11) J.-R. Liu, M. Itoh, M. Saito, T. Horikawa, and **K. Machida**, “Magnetic Properties and Electromagnetic Wave Absorption of -Fe/Z-type Ba-ferrite Nanocomposites,” *Appl. Phys. Lett.*, **88(6)**, 062503/1-062503/3 (2006).
12) W.-F. Liu, S. Suzuki, D. S. Li, and **K. Machida**, “Magnetic Properties of Fe-Pt Rich-film Magnets Prepared by RF Sputtering,” *J. Magn. Magn. Mater.*, **302(1-2)**, 201-205 (2006).
13) W.-F. Liu, S. Suzuki, D. S. Li, and **K. Machida**, “Magnetic Properties of Nd-Fe-B Film Magnets Prepared by RF Sputtering,” *J. Magn. Magn. Mater.*, **302 (1)**, 201-205 (2006).
14) W.-F. Liu, S. Suzuki, and **K. Machida**, “Orientation and Magnetic Properties of the Thick Multilayered $[NdFeB_x/Tb_y]_n$ Films,” *Jpn. J. Appl. Phys.*, **46(7A)**, 4113-4116 (2007).

15) J. R. Liu, M. Terada, M. Itoh, T. Horikawa, and **K. Machida**, “Enhanced electromagnetic wave absorption properties of Fe nanowires in gigaherz range,” *Appl. Phys. Lett.*, **91(10)**, 093101/1-093101/3 (2007).
16) N. Watanabe, M. Itakura, N. Kuwano, D.S. Li, S. Suzuki, **K. Machida**, “Microstructure Analysis of Sintered Nd-Fe-B Magnets Improved by Tb-Vapor Sorption,” *Mater. Trans.*, **48**, 915-918 (2007).
17) M. Itoh, K. Nishiyama, F. Shogano, T. Murota, K. Yamamoto, M. Sasada, and **K. Machida**, “Recycle of Rare Earth Sintered Magnet Powder Scraps as Electromagnetic Wave Absorbers in Gigahertz Range,” *J. Alloys Compd.*, **451**, 507-509 (2008).
18) K. Miura, M. Itoh, and **K. Machida**, “Extraction and recovery characteristics of Fe element from Nd-Fe-B sintered magnet powder scrap by carbonylation,” *J. Alloys Compd.*, **466**, 228-232 (2008).
19) K. Miura, M. Itoh, and **K. Machida**, “Surfactant-Assisted Preparation and Magnetic Properties of Iron-Based Nanowires,” *Jpn, J. Appl.Phys.*, **47(8)**, 2342-2344 (2008).
20) M. Itoh, K. Miura, and **K. Machida**, “Extraction of Rare Earth Elements from Nd-Fe-B Magnet Scraps by NH_4Cl,” *Chem.Lett.*, **37(3)**, 372-373 (2008).
21) D.-S. Li, S. Suzuki, T. Kawasaki, and **K. Machida**, “Grain Interface Modification and Magnetic Properties of Nd-Fe-B Sintered Magnets,” *Jpn. J. Appl. Phys.*, **47(10)**, 7876-7878 (2008).
22) M. Itoh, K. Miura, and K. Machida, “Novel rare earth recovery process on Nd-Fe-B magnet scrap by selective chlorination using NH_4Cl,” *J. Alloys Compd.*, **477**, 484-487 (2009).
23) D.-S. Li, S. Suzuki, T. Kawasaki, and **K. Machida**, “Grain Boundary Phase Formation and Magnetic Properties of NdFeB/Nd Multilayer Films,” *Jpn. J. Appl. Phys.*, **48(11)**, 033002-1-3 (2009).
24) M. Terada, M. Itoh, J.-R. Liu, and **K. Machida**, “Electromagnetic wave absorption properties of Fe_3C/carbon nanocomposites prepared by a CVD method,” *J. Magn. Magn. Mater.*, **321**, 1209-1213 (2009).
25) D.S. Li, M. Nishimoto, S. Suzuki, K. Nishiyama, M. Itoh, and **K. Machida**, “Coercivity enhancement of Nd-Fe-B sintered magnets by grain boundary modification via reduction-diffusion process,” *J. Phys. Conf. Ser.* , **150**, 012020-1-4 (2009).
26) N. Watanabe, H. Umemoto, M. Ishimaru, M. Itakura, M. Nishida, and **K. Machida**, “Microstructure analysis of Nd-Fe-B sintered magnets improved by Tb-metal vapour sorption,” *J. Microscopy,* **236(2)**, 104-108 (2009).

Also, I have published several decades papers in this research fields.

Additonally, I reported the research works as invited or contributing speakers at the following international meetings:

1) 9th Joint MMM/Intermag Conference, Anaheim, California, January 5-9, 2004.
2) The IEEE International Magnetics Conference, Nagoya, Japan, April 4-8, 2005.
3) The IEEE International Magnetics Conference, San Diego, California, May 8-12, 2006.

5. The additional research works related to this application.

We investigated the relationship between the content of Dy and/or Tb and magnetic parameters for a series of Nd-Fe-B sintered magnet pieces with the dimensions of 3 x 3 x 3 mm, which were supplied by Shin-Etsu Chemical Co., Ltd. The elemental analysis data and magnetic parameters measured on them without any treatment with Dy or Tb metals are listed in Table 1. Shin-Etsu Chemical Co. provides a number of Nd-Fe-B sintered magnets with various contents of Dy or Tb in order that the magnetic parameters, remanence (Br), coercivity (iHc), and energy product (BHmax) values are designed for the individual users in many application fields.

Table 1. The Dy or Tb metal contents and magnetic properties for a series of Nd-Fe-B sintered magnet pieces (untreated) produced by Shin-Etsu Chemical Co. with dimensions: 3 x 3 x 3 mm

Product Type	M (mass %)			Magnetic Properties		
	Dy	Tb	Total	Br (T)	iHc (MA/m)	(BH)max (kJ/m^3)
N52	0.59	0.67	1.26	1.446	0.993	380.4
N50M	1.05	0.61	1.66	1.422	1.206	378.0
N48H	2.36	0.56	2.92	1.403	1.435	370.3
N44MH	4.13	0.04	4.17	1.330	1.621	324.7
N43TS	4.66	0.81	5.47	1.298	2.036	324.4
N42SH	4.93	0.05	4.98	1.293	1.941	315.5
N41TU	4.75	2.10	6.85	1.261	2.352	301.5
N39UH	4.86	1.53	6.39	1.256	2.245	302.2
N36UH	4.94	1.57	6.51	1.214	2.182	323.8
N36Z	7.35	0.99	8.34	1.201	2.462	283.3
N32EZ	9.37	0.97	10.54	1.121	2.907	245.0

As described in this application sheets, we have invented the effective method to enhance the coercivity of the Nd-Fe-B sintered magnets without lowering the remanence values by introducing of Dy or Tb to the inside of such magnet pieces through the selective inner diffusion along the Nd-rich grain boundary region surrounding the Nd-Fe-B primary magnet phase. The magnet pieces were treated according to the same methods using the sputtering apparatus, especially, after carefully pre-evacuating below 1×10^{-4} Pa (7.5×10^{-7} Torr) to avoid the further serious oxidation of magnet pieces. The elemental analysis data and magnetic parameters measured on the Nd-Fe-B sintered magnet pieces treated with Dy or Tb metals are listed in Table 2.

Table 2. The Dy or Tb metal contents and magnetic properties for a series of Nd-Fe-B sintered magnet pieces treated with them at 950°C for 2 h in a purified Ar gas

Product Type	Run No	M (mass %)			Magnetic Parameters		
		Dy	Tb	Total	Br (T)	iHc (MA/m)	(BH)max (kJ/m^3)
N52	Dy-1	1.55	0.65	2.20	1.419	1.413	387.7
	Tb-1	0.65	2.01	2.66	1.401	1.812	371.6
N50M	Tb-2	1.01	2.11	3.12	1.362	1.977	366.9
N48H	Tb-3	2.38	1.25	3.63	1.398	2.058	378.9
N44MH	Tb-4	4.18	0.67	4.85	1.301	2.277	322.1
N43TS	Tb-5	4.59	1.42	6.01	1.296	2.633	328.2
N42SH	Dy-2	5.79	0.07	5.86	1.275	2.291	322.0
	Tb-6	5.01	1.62	6.63	1.263	2.729	312.9
N41TU	Tb-7	4.67	2.56	7.23	1.248	3.065	307.5
N39UH	Tb-8	4.91	2.20	7.06	1.249	2.948	307.7
N36UH	Tb-9	4.98	2.08	7.07	1.241	2.915	300.6
N36Z	Tb-10	7.25	1.66	8.91	1.198	3.271	287.7
N32EZ	Tb-11	9.22	1.57	10.79	1.090	3.788	235.8

From Table 1, one can see that the coercivity values are effectively increased with the amounts of the Dy and/or Tb metals by diffusing to the inside of magnet pieces. Also, it is clear that the Br and iHc values for untreated and treated magnets are fairly classified on the basis of the iHc and Br values defined by two equations:

iHc (MA/m) > or = 1 + 0.2 x M (mass%)

Br (T) > or = 1.68 - 0.17 x iHc (MA/m)

This critical difference between the magnetic parameters of the untreated and treated magnets is apparently based on the significance and domination of the present invention.

In Fig.1, the Br values are plotted against the iHc ones for the untreated and treated magnets and herein the critical borderline to classify them is given by a solid line in black.

A series of commercially available Nd-Fe-B sintered magnets are effectively improved to the coercive magnets useful for electric vehicles or hybrid-type electric

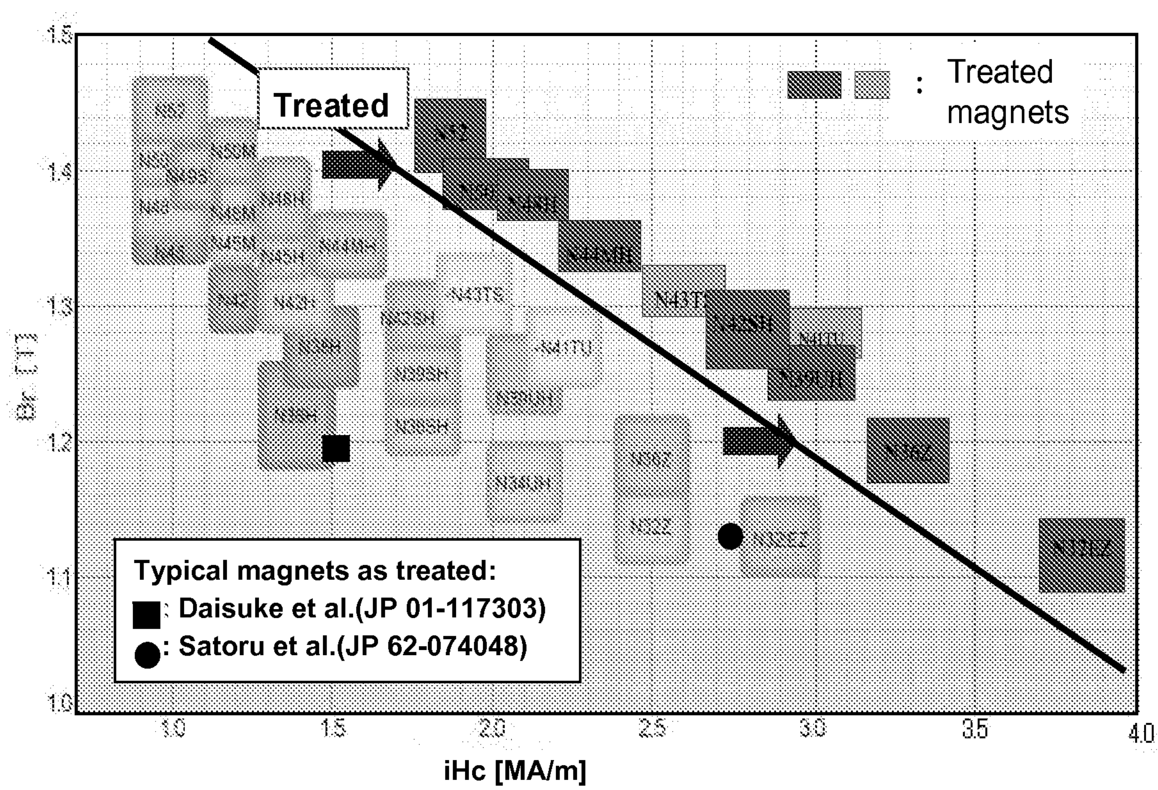

Fig. 1. The remanence versus coercivity plots for a series of the untreated and treated Nd-Fe-B sintered magnets with the sputtered Tb metals (see Table 2). The solid line represents the critical limitation to produce the high-performance magnets according to the conventional metallurgical technique.

(JP62-74048) also invented the surface modification methods, but their modified magnets never give any magnetic parameters above the critical borderline presented in Fig. 1. This means that their methods are different from ours in the essential point to produce the useful coercive permanent magnets by saving the expensive and short- supplying Dy or Tb metals.

This modification technique is strongly dependent on the diffusive characteristics of Dy or Tb elements through the Nd-rich grain boundaries toward the inside of magnet pieces. However, the Dy or Tb metals are easily oxidized even in the atmosphere containing a trace amount of O_2 or H_2O vapor. Therefore, one must carefully control the atmosphere to introduce the Dy or Tb metals on the surface and inside of magnets. Particularly, the heating process to diffuse the metals to the inside of magnets should be performed under a clean vacuum below 1 x 10^{-5} Pa (7.5 x 10^{-7} Torr) or inert gas like Ar.

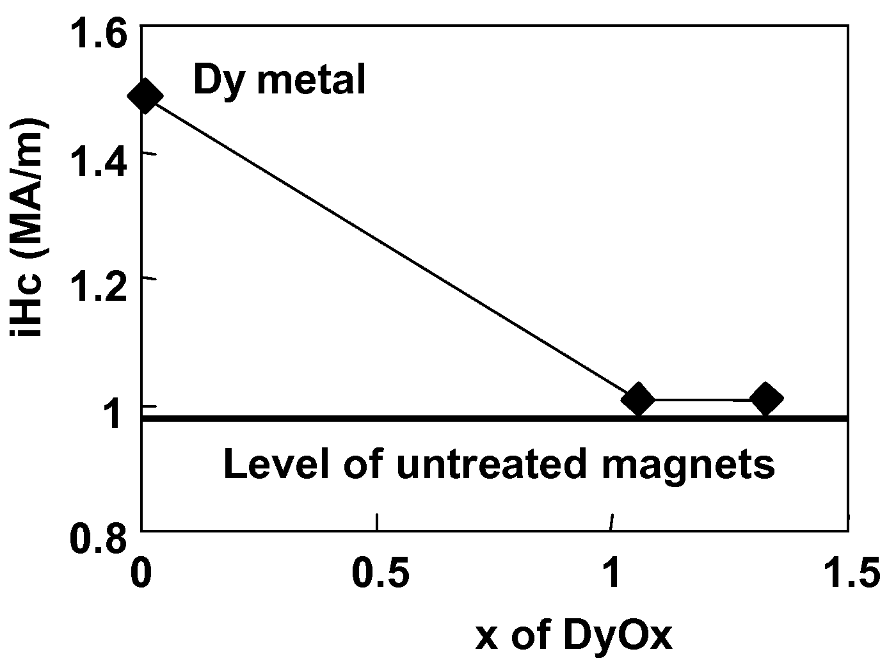

Fig. 2. Oxygen concentration dependences on the coercivity of Nd-Fe-B sintered magnets treated with conventional sputtered Dy metal or the DyOx species derived from the sputtered Dy metal. The solid line represents the typical coercivity level of the commercially available magnet (N52).

The reduced dysprosium oxides, DyOx (x=1.06 and 1.34) were prepared by pre-heating the sputtered Dy metals under the evacuated condition of 5 x 0^{-6} Torr (6.67 x 10^{-4} Pa) using an oil diffusion pump at 500°C for 5 or 20 min, where the film thickness of Dy metal was 3 μm for 6 square planes of magnetic pieces (3 x 3 x 3 mm). The heating for improving the coated magnet pieces was made under the conditions: at 900℃ for 1 h in a purified Ar atmosphere. The iHc value of Dy_2O_3 was adopted from the data given in Fig.2. The oxygen content of DyOx was analyzed on an oxygen/nitrogen analyzer. It is concluded that the DyOx has a limited effect on the coercivity enhancement of Nd-Fe-B sintered magnets. Therefore, the background pressure (< or = 1 x 10^{-4} Pa) of vacuum chamber and the purity of Ar atmosphere (< several tens ppm of O_2 or H_2O) are considerably important.

The undersigned declares that all statements made herein of his/her own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date April 30, 2010

Signature Kenichi Machida

Ken-ichi Machida
(Professor of Osaka University)